BROWN

An Investigation on the Behavior of the Selenium Cell with Special Reference to the Effect of Pressure on the Electrical Resistance

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AN INVESTIGATION ON THE BEHAVIOR OF THE SELENIUM CELL, WITH SPECIAL REFERENCE TO THE EFFECT OF PRESSURE ON THE ELECTRICAL RESISTANCE

BY

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This is to certify that the thesis prepared under my supervision by

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entitled AN INVESTIGATION ON THE BEHAVIOR OF THE SELENIUM CELL, WITH SPECIAL REFERENCE TO THE EFFECT OF PRESSURE ON THE ELECTRICAL RESISTANCE

is approved by me as fulfilling this part of the requirements for the Degree of Master of Arts

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Selenium was discovered in 1817 by Berzelius. It belongs to the same group of elements as sulphur and tellurium. Like the other members of its group it exists in allotropic forms. It is called a metalloid. In one form it is as good a non-conductor of electricity as many of the so called insulators. In another form its conductivity is almost equal to that of such metals as iron and mercury.

In 1873 W. Smith(Am.J.Sci. 5,301) was using selenium as a high resistance in telegraphic work, when he accidently discovered that selenium changed its resistance to electric current when light fell upon it. Since the time of Smith a number of men have published results of investigation with the form of selenium which changes resistance with change in intensity of illumination, but no one has reached a satisfactory and conclusive explanation of why there should be a change of resistance of selenium upon illumination. The decrease of resistance is as much as ten times under favorable conditions and recently Adolph(Technics, Feb.1905) seems to have reached a limit of fifteen times. This seems remarkable when we remember that it is doubtful if the slightest change of resistance takes place in ordinary conductors when they are illuminated.

For a number of years it has been customary to say

that a "selenium cell" changes resistance rather than to say that selenium changes resistance, because it has not been certain whether the selenium itself changes resistance or whether the change of resistance takes place in the contact layers between the selenium and the metal electrodes. A "selenium cell" then is generally known as any device by which two like or unlike metals are connected by sensitive selenium. By sensitive selenium is meant that crystalline form which changes resistance upon illumination.

The explanation of the decrease of electrical resistance when light falls on selenium, we may choose to call the "selenium question". The purpose of this paper is to set forth the results of investigation, which it is hoped will be of value in the solution of the question. These results were presented to the February 1905 meeting of the American Physical Society by Professor A. P. Carman.(Phy. Rev.Mar.1905).

The first men to verify the discovery of Smith were Sale(Proc.Roy.Soc. 21, p 285) and Rosse(Phil.Mag.1874,167). However they did not add anything particularly new in the investigations.

One of the best investigations on the subject, was begun by Siemens in 1874(Pogg.156,334-335),(Dingl.POL.J.1875, 217,61-63)(Wied.2,534)(Life & Works of Werner von Siemens). He thought he found selenium to exist in four forms. The amorphous or commercial form, a second form which exists only at 200 to 215 degrees C., a third form which is crystallized at 80 to 150 degress C., a fourth form which is crystallized by about ten hours of heating at 200 degress C. The last two

forms were most sensitive to light, especially the last which decreased resistance as much as ten times upon illumination. Increase in temperature of the form crystallized at 200 degrees C. had the same effect as upon metals. The higher the E.M.F. used with this form, the higher was the resistance, while the form crystallized below 150 degrees C. decreased resistance when exposed to light or heat, or when the E.M.F. was increased. In one cell he found the resistance to decrease almost uniformly until the conductivity had increased a thousand times as the E.M.F. increased. Siemens found the decrease of resistance due to light, heat and high voltage was only temporary, most of the resistance being regained in a few minutes after the light or high voltage was removed. He makes special mention of the fact that the alteration of resistance due to increase of current was always in the same direction as if the cell were heated by the current. Very great cooling destroyed the crystalline form at 200 degrees C. He found further:

"That different sized electrodes in the same cell made a difference in the resistance depending upon the direction of the current."

"That whenever selenium gave up its latent heat there was a marked change in its resistance, the influence of the latent heat being nearly twice as great as that of free heat."

What Siemens thought as to the selenium question is shown in the following quotation:(Life & Works of Werner von Siemens) I pg 235

"Now to explain from this point of view the peculiar and contradictory phenomena, which were observed with modification "C"

(crystallized at 200 degrees) which according to it is to be considered as a solution of metallic selenium in crystalline selenium, one must assume that the essential part of the resistance of the selenium has its seat at the boundary layers of the surfaces of contact and that the layers are altered electrolytically by the current".

About the same time, Adams and Day(Pr.Roy.Soc. 23, 535,25, 3) did considerable work on selenium. They made cells with resistance as low as 68, 58 and 55 ohms by heating in a sand-bath. These cells when prepared by heating in air, had a resistance as high as 7,000,000 ohms. These low resistance cells were very unstable, for light or jarring of table increased resistance from 58 to 5600 ohms. Adams and Day concluded that change of resistance was due to electrolytic effect; (1) because resistance of a selenium bar changed with the E.M.F.; (2) because the passage of a battery current was always followed by polarization; (3) because change of direction of current changed resistance.

Draper and Moss(Ch.N.33,1) distinguished three varieties of crystalline selenium. So far as they knew but one of these was sensitive to light.

In 1874 Rammelsberg(Pogg.Ann.152,15-157) worked on the varieties of selenium. He concluded that there were four forms, three of which were crystalline.

Moser(Phil.Mag.12,212) thought that the variable resistance was due to variable contact, because of the low specific resistance of selenium compared to that of the selenium cell. He was able to get cells varying from 700 to

300,000 ohms, depending on the way the selenium was crystallized.

Perhaps no one has done more work on the selenium question than Shelford Bidwell(Ch.N.43,105)(Phil.Mag.15,31-35)(Ch.N.51,26&310)(Phil.Mag.20,178)(Ch.N.52,192)(Phil.Mag.31,250)(Beibl.5,607). Certainly no man has been referred to in the literature as much as he on the subject. He started a great deal of work by the statement, "I am inclined to think that pure selenium would be a perfect insulator." He found that sulphur cells were sensitive to light and heat; that sulphur and graphite melted together was a fair conductor; that shellac and graphite melted together was a non-conductor. He concluded that change of resistance upon illumination was due to a selenide because:

(1) The resistance diminished when the cells were annealed; (2) the kind of metals used as electrodes affected the resistance of the cell; (3) the resistance decreased with battery power; (4) slight increase of temperature produced great change of resistance; (5) the resistance greatly diminished in time.

He said that the selenide was formed in two ways, either by the uniting of the selenium with the electrode or with impurities found in the selenium.

Townsend(Electrician Oct.7,1900) found that selenium was sensitive to light only within a certain range of temperature, about atmospheric temperature. Like many other experimenters he was led to work on selenium with the idea of constructing an absolute photometer, which would do away with the

personal error. He found that it was not the actinic rays which affect selenium most, but those which produce the greatest heating effect.

Pfund(Jan.1904, Phil. Mag.)and Berndt(Beiblaette 1904) found that pure selenium on carbon electrodes gave cells just as sensitive and more constant results than those prepared according to Bidwell's description. They conclude, separately, that since selenium does not unite with carbon, the action of light on it is not due to the formation of a selenide. Pfund found that light waves of 73 μ have the greatest effect upon the resistance. He thinks that the change produced by light is a change in the selenium itself.

Fritts(Am.J.Sc.26,465,472) and Righi(Wied.Beibl. 12,683) and Uljanin(Wied.Ann.34,241,273) found that certain cells not only changed their resistance but that they even produced a current when exposed to light. Fritts offered no other explanation than that there was some close relation existing between light and electrical energy.

Himstedt(Ann.der Phy.1901) has shown that radium rays change the resistance of selenium cells the same as light and heat and Roentgen says, but that the change is slower and by no means as marked.

Russel(Proc.Roy.Soc.64,407) found that hydrogen peroxide gave off, as he stated it, an emanation which reduced the resistance of selenium cells.

Agostini(Beiblaetter 1899) found electric waves to decrease the resistance of selenium cells slightly.

That the sensitiveness of selenium does not depend upon it being heated with the electrodes, was proved by

Uljanin(Wied.34,241) when he placed steel electrodes in a plate of tempered selenium. The resistance was descreased nine times upon illumination. He also found this cell to produce an E.M.F. proportional to the illumination.

Bidwell, and later Anzel(Beibl.1904, p 723) investigated tellurium, which belongs to the same chemical group as sulphur and selenium. The resistance of tellurium is even higher than that of selenium, thus making it even more difficult to work with than selenium. In both cases however the resistance of tellurium decreased slightly when the light fell upon it.

Saunders(Phy.Chem.4,428,515) from the standpoint of the chemist, carried on an investigation to determine the allotropic forms of selenium. He concluded that selenium existed in three allotropic forms, the liquid form, including the vitreous, amorphous and the soluble selenium, the red crystalline form and the gray crystalline or metallic form.

By dilatometric measurements he showed the metallic form to be stable up to about 220 degress C. showing no tendency below that to go over into any other form. The vitreous selenium remains unaltered for years but it goes over into the metallic form at 60 to 80 degrees C. A large number of liquids transform amorphous selenium catalytically into the red crystalline variety. Another group changes it into the metallic form, while a third group of liquids such as water and aqueous solution have no influence. He describes experiments which make it probable that the red crystals have an unstable melting point at 170 to 180 degrees C. It seems from his results that

there are not as many crystalline varieties as the early experimenters thought. The Bibliography of Saunders is the most complete that can be found on the subject.

The foregoing reviews the work that has been carried on up to the present time bearing more or less directly upon the selenium question. The experimental results on selenium vary even more than is indicated in this paper. Consequently there have been different theories as to why selenium decreases resistance when illuminated. There are perhaps two reasons for these different results. First, the number of amorphous forms of selenium and the properties of each, physical and chemical, has been and is yet quite unsettled. Second, experimenters in many cases have not stated all the conditions, which were determining factors in getting their results. The latter is perhaps due to the lack of knowledge about selenium itself.

It might not be out of place here to state that the light effect on selenium is of practical importance as well as theoretical interest. Hammer(Trans.Am.Inst.E.E.May 1903) gave a very interesting talk before the Institute of Electrical Engineers, in which he described the kinds of selenium cells and their possible uses in wireless telephony, light and heat regulators, fire and burglar alarms, radiophone, photographone, etc. He mentions a number of firms that make selenium cells which may be used for the above purposes. Ruhmer of Berlin is perhaps the most successful in making such cells. By the use of a selenium cell in a vacuum he has been able to send messages by light rays a distance of nearly ten miles. All

the cells of which we have any record, have been made very largely by "cut and try" methods. If we knew why selenium changes resistance when illuminated, it is not unreasonable to suppose that we could improve that property of a selenium cell which makes it change its resistance when illuminated, in which case it would be possible, to send telephonic messages a much greater distance than ten miles by that means.

Most of the cells used in this investigation were made after directions given by Bidwell (Phil.Mag.31,251). About 25 cells were made by the writer. The following is a description of those cells which were investigated under high pressure and other extraordinary conditions.

In cell 2, several sheets of mica were fastened together with shellac. The resultant mica sheet about 2 x 3 centimeters was placed between two strips of wood. The wood was then put in a lathe and turned down flush with the mica and until the wood and mica was 1.5 centimeters in diameter. Then threads were cut on the wood and mica 30 to the inch. After it was removed from the wood, two number 36 copper wires were wound parallel to each other on the mica. The vitreous selenium, about one gram, was melted on one side of the wire grating at about 220 degrees C. The selenium was not finely powdered before melting. After sudden cooling it had a dark shining lustre, and its resistance was almost infinite. The grating and the selenium was then kept at about 135 degrees C. until the selenium crystallized. It was then a dull gray color. After crystallization it was raised to about 200 degrees C. and kept there for three hours. Two hours were allowed for

the grating or cell to cool. Its resistance was then about 75,000 ohms in the dark.

Cell 3 was made similarly except that each of the two electrodes were wound around the mica strip only twice and the electrodes were made of number 20 copper wire pounded out flat so that they were about 4 mm. wide. After being crystallized the cell was not kept at 200 degrees C. for several hours but was merely heated a little above 150 degrees and slowly cooled. When completed it was mostly a shining gray. The selenium came off of one of the middle electrodes, showing a dark coating on the copper. At first its resistance was 30,000 ohms at room temperature, but the next day its resistance was 70,000 ohms.

After ten days the resistance was fairly constant at 145,000 ohms. This cell had a resistance below that of the average normal cell. Its increase of resistance is similar to that observed by Adams and Day and Moser.

Cells 4 and 4a were made as a single cell, like 2 and 3 but when annealed the resistance was only about 7,000 ohms. As the two halves of the cell were slightly different in color, it was cut in two making one cell of resistance 7,000 ohms and another 4a of 1,900,000 ohms at 14.8 degrees C. when 3 volts was used in the circuit. But when 20 volts was used 4a had only 1,200,000 ohms resistance. The electrodes were of flattened wire 1 mm. wide and 1 mm. apart. After three months the resistance of cell 4 had increased to 10,900 ohms.

In cell 5, the electrodes were made of copper wire, .4 mm. diameter flattened out so as to be about 1.5 mm. wide.

Two of these copper strips were wound parallel around a strip of mica 2.3 x 7 cm. There were in all twenty turns. Vitreous selenium was melted on one side of this copper grating at a temperature somewhat above 217 degrees C. It was then cooled and afterward kept at a temperature anywhere from 130 to 210 degrees C. for several hours. The cell was peculiar in that it was very hard to anneal, that is to change it over from the lustrous vitreous form to the crystalline form. In fact when the cell was completed, three forms of selenium were recognizable. About one- half the cell was of a somewhat shining gray while the rest was partly of coarse reddish crystalline structure and partly vitreous. However the behavior of the cell was very much like that of many others. In the dark at 22 degrees the resistance was 85,700 ohms for several weeks after being made. But after being subjected to temperatures as low as - 65 degrees C. the resistance rose to 120,000 ohms where it seemed to be quite stable.

The construction of cell 6 was about like that of the others, except that number 36 platinum wire was used as electrodes and the selenium was melted on both sides completely covering the electrodes. The area covered by the selenium was 2 x 2 x 25 cm. At first the resistance was 5,000,000 ohms in the dark, but this was too high for easy working, so more selenium was put on and its resistance was then, after annealing, 1,400,000 ohms at 19 degrees C.

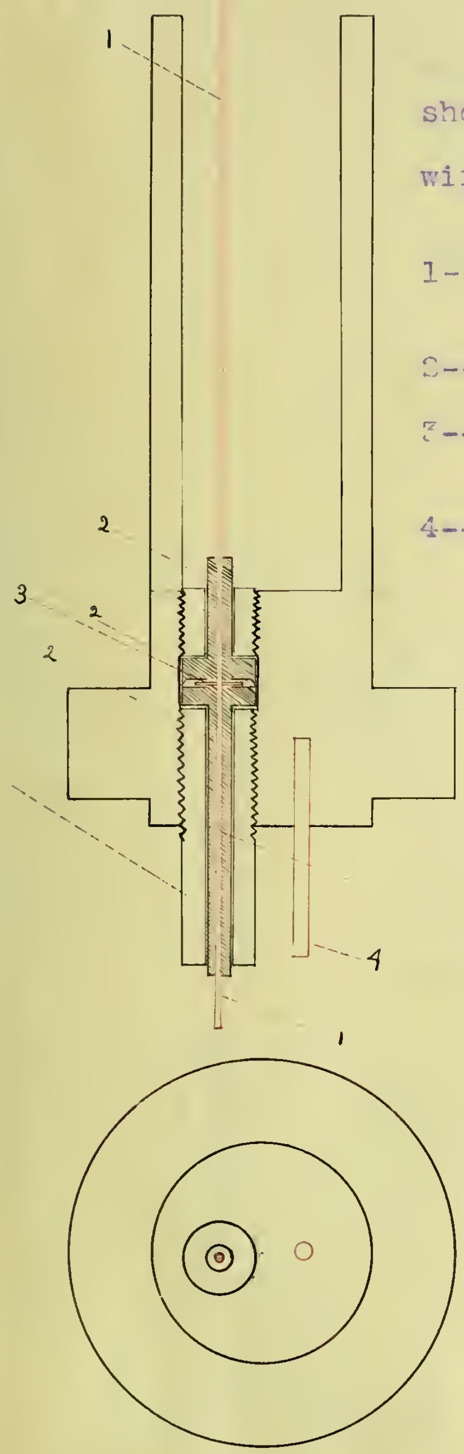
In cell 7 there were 8 turns of copper wire to the centimeter, making a total of 32. About 6 grams of selenium was put on the grating after it had been heated beyond the

melting point of the selenium. The resistance was infinite when hard but shortly, after annealing, the resistance was only 2,900 ohms. Two months later the resistance had fallen to 600 ohms. It was then cut in two when one part had a resistance of about 700 while in the other part the resistance was 1,000,000 ohms.

The resistance of the selenium cells was measured by the Wheatstone bridge method, usually with a single dry battery in the circuit.

Hydraulic pressure was obtained by a Cailletet pump, with extra piston and needle valves, by which the pressure could be maintained constant for sometime, designed by Professor A. P. Carman. The cell whose resistance was to be measured was placed in kerosene in a receiver connecting with the pump. One of the difficulties of the investigation was to get connecting wires through the receiver to the selenium cell with perfect insulation and at the same time to be rigid enough to stand 700 atmospheres. Resinous insulators would not do when kerosene was used in the receiver. Finally a method of insulation was arrived at modeled after that of Knipp(Phy.Rev.11,133). As shown in Fig. 1, only one wire was insulated.

Although the object of this paper is to set forth facts which might have weight in answering the selenium question, yet the chief stress will be laid on a newly discovered property of selenium, the change of resistance with pressure. While the author has repeated considerable of the work of other experimenters on the resistance of selenium, only brief mention will be made to causes other than pressure which decrease the resistance



PLUG of RECEIVER

showing method of insulating

wires leading to SELENIUM CELL.

1---- insulated wire leading to galvanometer from above, to selenium cell below.

2---- hard rubber

3---- copper disc soldered on wire(1)

4---- non-insulated wire from galvanometer to cell, galvanometer being fastened to plug.

fig. 1

of selenium.

As soon as one of the cells was placed under pressure there was a change in resistance. If this result remained constant, there were only four possible explanations that suggested themselves. The resistance of the kerosene might change with pressure. The kerosene when under pressure might give some radiation which would change the resistance of the selenium. Work was done on the selenium and the kerosene and thereby heated it. Since heat affects the form of cell that I had the same as light does and the same as pressure did, it was evident that a part if not all of the effect was due to heating. Then there was the fourth possibility that in some way the pressure changed the resistance of the selenium cell.

One complete set of readings was sufficient, as will be seen later, to prove that nothing more than a neglible error could come in from change of resistance of insulation, or of conducting wires.

A. B. Griffiths(Sc.Ab.7,102) found that certain plant and animal tissues give off radiations which slightly decrease the resistance of selenium. Since radium also had been found to decrease slightly the resistance of selenium, he thought animal tissues perhaps gave out the same kind of radiations that radium does. But when one thinks of the number of conditions that alter the resistance of selenium he will be a little slow to ascribe any decrease of resistance to radiations from tissues. I found that if a selenium cell was wrapped in five thicknesses of black paper such as surrounds photograph plates to keep out the light, it would change the resistance slightly if .1 grams of radium of 30,000 activity were laid near it by

the hand. But when the radium was brought near by a long string and pole, there was no perceptible effect. Also there was no effect if there was a sheet of glass or metal over the cell when the radium was brought near. Apparently it was the heat radiations from the hand rather than from the radium that changed the resistance. This does not mean that cells prepared differently when exposed to radium rays would not show an effect. If we conclude that radiations from animal tissues are too much like N rays at present to be given any weight, it seems that so far as observed the effect of any radiation on selenium is in some way proportional to the heating effect of that radiation. Howver the resistance of a selenium cell decreased 30% when brought 5 cm. from hydrogen peroxide. But as no substance could be found through which this radiation would pass, it was concluded that it was not a radiation. Besides it was not transmitted in straight lines. If the hydrogen peroxide was only partly covered, the resistance was still effected. It seemed safe to say that no N rays or any other ether rays were produced by the compression of the kerosene which would produce any noticeable effect on the selenium.

The next step was to find out how much of the change of resistance was due to heating and how much if any was due to mere compression. It was thought best to find out the rate of cooling of the kerosene and receiver after it was heated by compression. The following method was used. Copper is known to change very little if any under pressure. So a coil of No. 40 silk covered copper wire was placed in the hard rubber case shown in Fig. 2 which in turn was placed in the kerosene of

the receiver. The receiver was placed in tap water fairly constant at 13.4 degrees C. The coil had a resistance of 39.51 ohms at 13.4 degrees C. After the resistance of the coil had become constant it was assumed that the temperature of the kerosene was the same as that of the tap water. Then the pressure was raised to 425 K.gm. per sq. cm. and maintained at 420 K.gm. until the coil had returned to the resistance that it had at atmospheric pressure. The resistance was measured at intervals shown in the following data. After the resistance was constant the pressure was suddenly lowered to zero and thereby cooled the kerosene and receiver the same amount that it had been heated previously by compression.

PRESSURE $\frac{K\ gm.}{cm^2}$	Ohms, resistance	Time P.M.	Temperature of tap water
0	39.51	8:20	13.4° C.
425	40.11	8:25	
420	39.95	8:27	
420	39.84	8:29	
420	39.74	8:30	
420	39.69	8:32	
420	39.61	8:34	
420	39.55	8:38	
420	39.54	8:40	
420	39.53	8:43	
420	39.52	8:48	
420	39.51	8:54	
420	39.51		

PRESSURE K.gm./cm.	RESISTANCE ohms	TIME P.M.
0	38.91	8:55
0	39.06	8:57
0	39.21	8:58
0	39.31	9;00
0	39:40	9:03
0	39.46	9:06
0	39.48	9:08

This data as shown in curve 1, Fig. 3, shows that in 34 minutes the temperature of the kerosene has returened to the temperature of the tap water, when the pressure was suddenly raised or lowered 420 atmospheres. By rough calibration one ohm change in resistance in the cell used signified about seven degrees C. in temperature. The curve shows that after 20 minutes the coil had returned to within .03 ohms of what it was at 13.4 degrees C. and that the temperature had returned to about 13.61 degrees C. After ten minutes the temperature would be 14.5 degrees C.

The first cell from which anything like conclusive results were obtained was (4a). When 1.4 volts was in the circuit the following readings were taken:

PRESSURE K.gm./cm.	RESISTANCE ohms	Temperature of tap water varying from 16 to 14.8° C.
450	650,000	
270	1,300,000	
350	1,100,000	
320	1,200,000 after 10 min.	
220	1,440,000 after 40 min.	

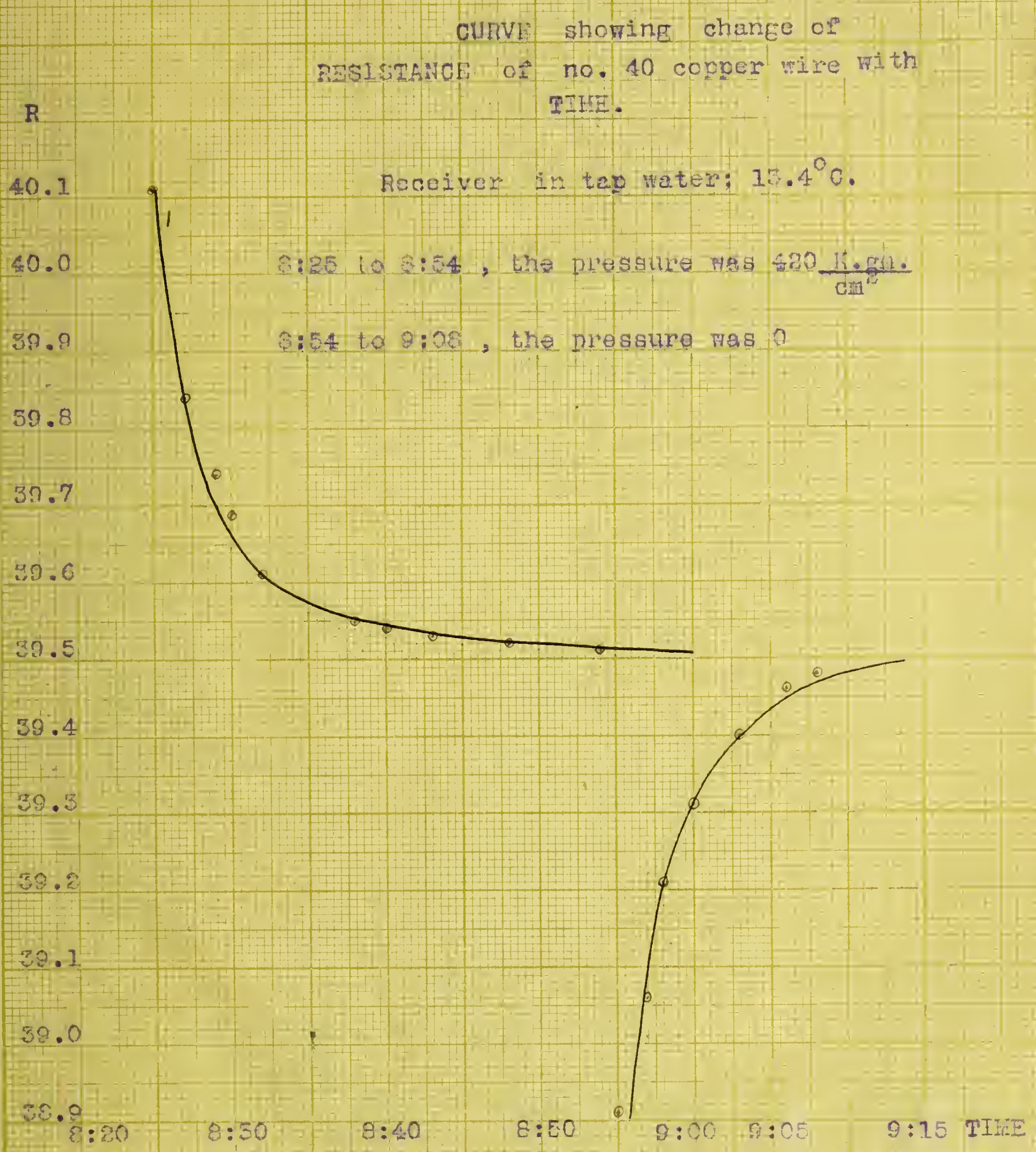

CURVE showing change of
RESISTANCE of no. 40 copper wire with
TIME.
Receiver in tap water; 13.4°C.
8:25 to 8:54, the pressure was 420 K.gm./cm²
8:54 to 9:08, the pressure was 0
R
40.1
40.0
39.9
39.8
39.7
39.6
39.5
39.4
39.3
39.2
39.1
39.0
38.9
8:20
8:30
8:40
8:50
9:00
9:05
9:15
TIME

fig.3

PRESSURE $\frac{K.gm.}{cm.}$	RESISTANCE ohms
185	1,530,000
180	1,700,000
160	1,720,000
80	1,730,000
20	1,920,000
22	1,940,000
0	1,990,000 after 10 min.

When 10 volts was used in the circuit the resistance under pressure varied as follows:

PRESSURE	RESISTANCE
0	1,170,000
240	900,000
400	770,000
495	720,000
450	770,000
70	1,120,000
72	1,100,000
0	1,230,000
0	1,200,000 after 10 min.

The curves 2 and 3 in fig. 4 show that the resistance decreases less under pressure when the voltage is high than when low. This seems to indicate that the current diminishes the resistance for the same reason that the pressure does.

The next cell that was tried was number 5. In this particular case the cell was wrapped in sheet rubber and placed

CURVE showing change of RESISTANCE of SELENIUM CELL (4a) with PRESSURE.

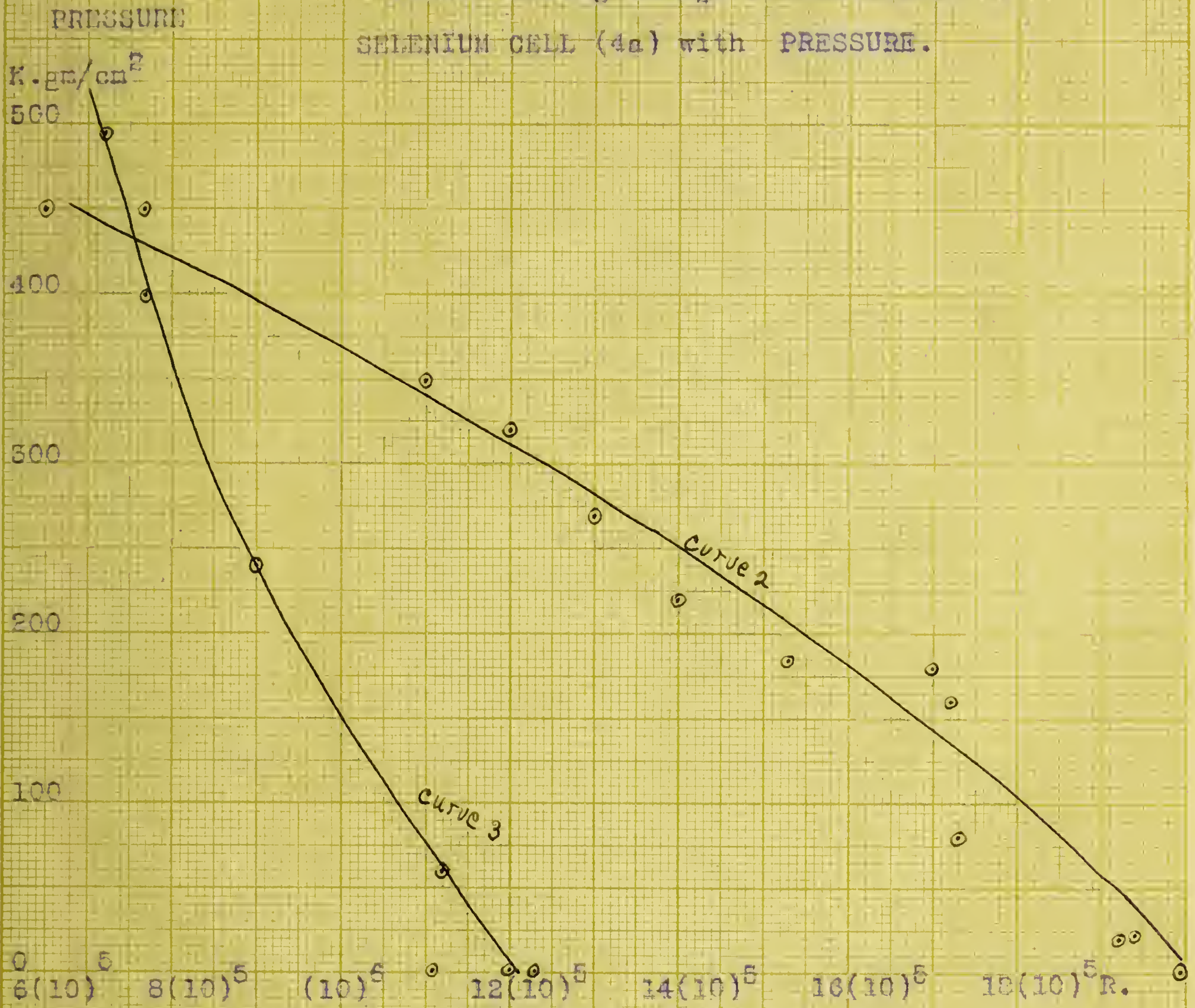


fig. 4

in the kerosene of the receiver. The receiver was placed in air at room temperature, 26 degrees C.

The readings were:

PRESSURE $\frac{K.gm.}{cm.}$	RESISTANCE ohms
0	79,000
0	79,900
40	75,000 after 10 min.
110	66,000 after 1 min.
65	72,000 after 10 min.
40	75,000 after 30 min.
200	55,400
250	47,000

This data is shown in curve 4, fig. 5.

Later cell 5 was tried again when the temperature of the surrounding air was 19.5 degrees C. The following are the readings which are shown graphically in curve 5, fig. 6.

PRESSURE K.gm.	RESISTANCE ohms	TIME OF OBSERVATION P.M.
0	103,000	2:50
333	59,500	3:54
158	81,700	4:10
580	39,000	4:16
30	106,000	4:35
528	43,000	

Again readings of resistance were taken on cell (5) when under pressure. This time the cell was surrounded inside the receiver by an open endglass tube. The receiver was packed in snow and ice, while the temperature of the room was 10° C.

Curve showing change of Resistance of

SELENIUM CELL with PRESSURE.

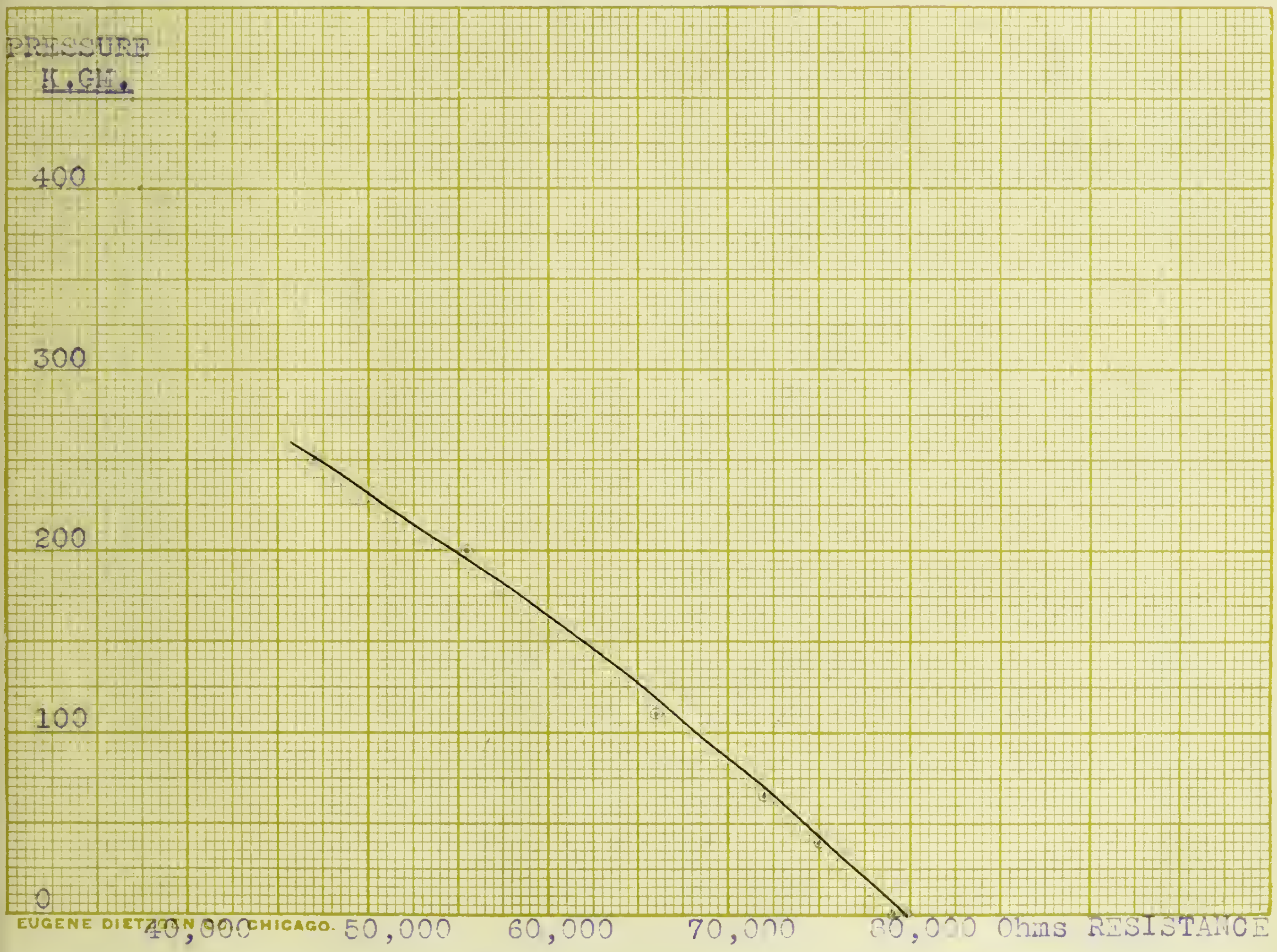


fig. 5

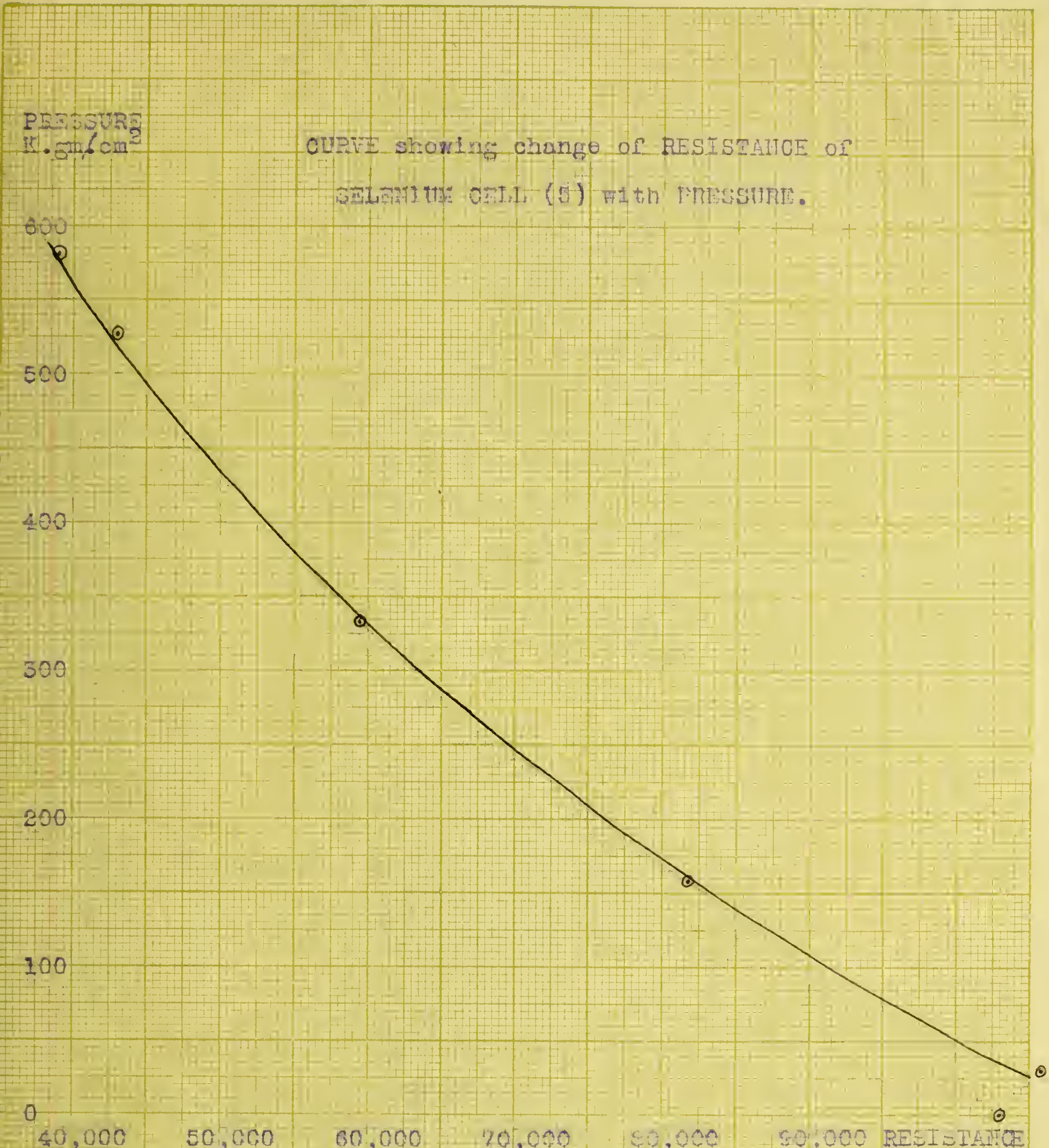

PRESSURE
K.gm/cm2
CURVE showing change of RESISTANCE of
SELENIUM CELL (5) with PRESSURE.
600
500
400
300
200
100
0
40,000
50,000
60,000
70,000
80,000
90,000
RESISTANCE

fig. 6

After the receiver had been packed thus for about four hours so as to reach a constant temperature, the following observations were taken at the time indicated.

PRESSURE K.gm./cm.^{2}	RESISTANCE ohms	TIME of observation.
218	63,900	1:17
150	72,400	1:20
151	72,300	1:26
150	72,300	1:28
150	72,510	1:30
120	pressure lowered	1:30 1/2
120	75,100	1:33
120	76,960	1:38
120	76,980	1:40
100	pressure lowered	1:40 1/2
99.5	80,000	1:44
100	79,900	1:45
100	79,790	1:49
70	pressure lowered	1:50 1/2
70	84,200	1:52
70	84,400	1:55
70	84,400	1:59
50	pressure lowered	2:00 1/2
50	88,400	2;02
50	87,900	2;07
50	87,800	2;09
30	pressure lowered	2:10 1/2
31	91,010	2:13
30	91,200	2:17
30	91,150	2:20
0	pressure lowered	2:20 1/2
0	96,200	2:23
0	96,140	2:25
0	96,340	2:33
0	96,000	2:37

The resistance at the end of ten minute intervals is plotted in curve 6, fig. 7. Later under like conditions cell (5) was put under pressure and the resistance noted as follows and as shown in curve 7, fig. 7.

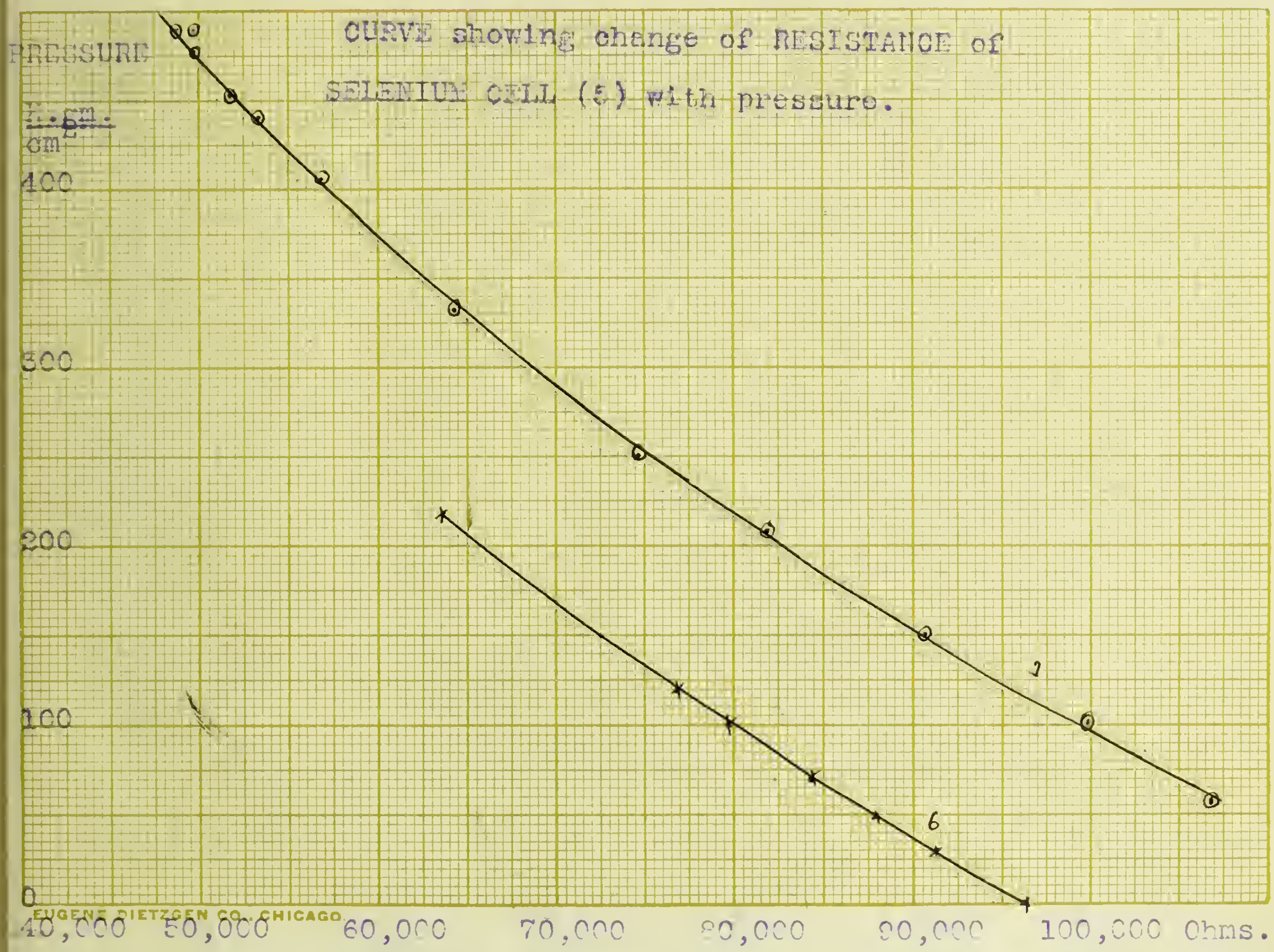

CURVE showing change of RESISTANCE of
SELENIUM CELL (5) with pressure.
PRESSURE
K.gm.
cm
400
300
200
100
0
7
6
EUGENE DIETZGEN CO. CHICAGO
40,000
50,000
60,000
70,000
80,000
90,000
100,000 Ohms.

fig. 7

PRESSURE K.gm./cm.^{2}	RESISTANCE ohms	TIME
490	44,600	2:52
496	44,600	2:55
570		2:57
530	42,400	2:59
490	48,700	3:15
478	49,700	3:20
453	51,700	3:38
440	53,100	3:45
405	56,800	4:15
333	64,330	4:25
250	74,600	4:30
208	81,900	4:35
150	90,500	4:39
102	99,900	4:44
59	106,900	4:47
0	115,000 112,000	5:18

There were two peculiar things observable in cell (5). There was no creeping effect, which causes more or less trouble to every one who experiments with selenium cells. The creeping effect in selenium cells is very much like polarization effects in galvanic cells. Another peculiar thing is that curves 6 and 7 should be so far apart and yet parallel. The first inference would be that it is due to temperature differences, but a short study of the data on the cell shows this to be impossible. Rather the explanation seems to be that in the cell the selenium is in a state of unstable equilibrium. There are a number of things that will destroy this equilibrium. As we

shall notice later, cooling to - 65 degrees C. destroyed it in one instance. Many experimenters have noted that time will destroy it. It seems here that after being released from high pressure the cell was in quite unstable equilibrium. The fact that the resistance varied so greatly at 0 pressure within one minute of time, as shown in last data, would indicate this.

The last cell that was tried for the pressure effect was number 6, the one with platinum electrodes. Creeping was very decided in this cell, so that it was difficult to get the resistance accurate to more than two significant figures. For each pressure two readings were taken of the resistance, one just after the temperature was constant, the other after the current had flowed a time. This gave the minimum and the maximum value of the resistance for each pressure, which are shown separately in the curves 8 and 9, fig. 8. The cell was placed in the hard rubber case previously spoken of. The receiver was placed in tap water which was quite constant at 15.1° C. The following are the readings taken:

PRESSURE K.gm./cm.	RESISTANCE Minimum	RESISTANCE Maximum	TIME P.M.
65	1,240,000	1,440,000	8:35
140	1,140,000	1,280,000	8:40
230	950,000	1,100,000	8:45
330	800,000	920,000	8:50
430	630,000	740,000	8:54
510	550,000	650,000	8:56
570	520,000	594,000	9:00
650	497,000		9:05

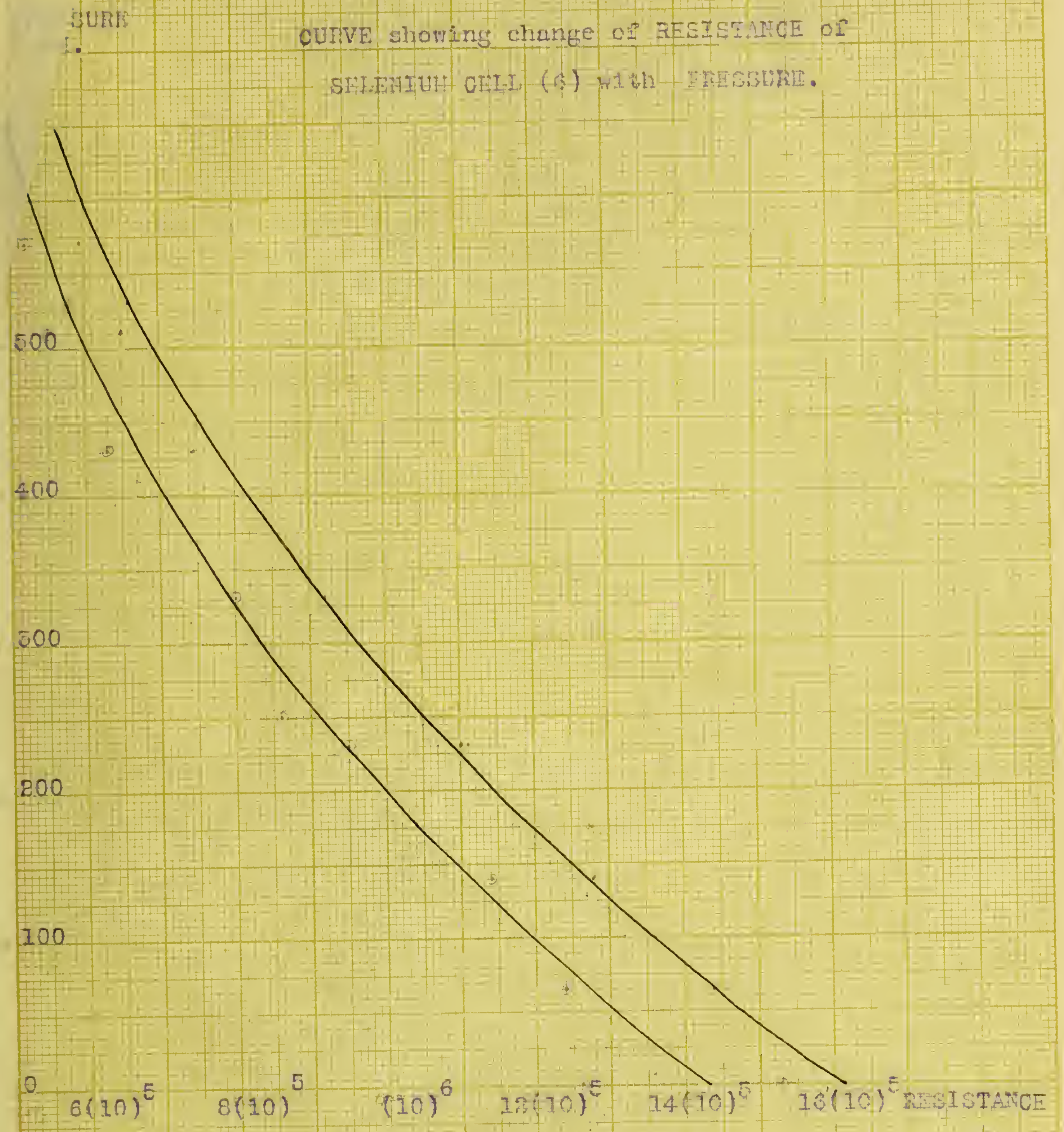

CURVE showing change of RESISTANCE of
SELENIUM CELL (6) with PRESSURE.
CURR
I.
500
400
300
200
100
0
6(10)^5
8(10)^5
(10)^6
12(10)^5
14(10)^5
16(10)^5
RESISTANCE

fig. 8

PRESSURE K,gm. cm.	RESISTANCE Minimum	RESISTANCE Maximum	TIME P.M.
530	580,000	660,000	9:10
250	860,000	1,220,000	9:15
0	1,530,000	1,670,000	9:17
0	1,260,000	1,610,000	9:22

Since after all it is the light phenomenon and not the pressure effect that is so peculiar, it is perhaps worth while to note the effect of light on one of these cells. However it may be stated here that the light effect on the cells used in these experiments was essentially the same as the effect of illumination on a cell made by Ruhmer and tested in the Physics Laboratory of the University of Illinois. The only apparent difference was that the Ruhmer cell was slightly the more sensitive to light.

Cell (5) was placed in kerosene in a test tube, which was surrounded by ice on one side. A 16 cp. incandescent lamp was used as a source of light.

RESISTANCE ohms	DISTANCE of light cm.
103,500	
77,500	30
66,400	20
58,400	12
55,400	10
47,400	5

The cell then returned to 85,400 ohms, at once, in dark. From curve 10, fig. 9, we see that the resistance varies as the distance. Since intensity of illumination varies in-

versely as the square of the distance, we conclude that the resistance varies as the square root of the intensity.

The light effect was tried again on the same cell, without keeping it at constant temperature. The lamp was placed on the stone pier so that it faced the selenium cell. The cell was fastened on the end of a paste board box so that it could be moved to and from the light. A thermometer was placed beside the cell and just in front of it so as to get an idea of the temperature of the cell. Curve 11, fig. 9, shows the resistance as the cell approached the light and curve 12, fig. 2, shows the same as the cell was taken away from the light. From the curves in fig. 9, one sees that the heating effect of the rays play no small part in the change of resistance. If we could get light rays which would produce no heating effect, it is very doubtful if we would get any change of resistance at all.

The data plotted in curves 11 and 12 are given below:

RESISTANCE	DISTANCE cm.	TEMPERATURE
85,000		
77,400	50	
74,900	40	
72,400	30	19.6° C.
67,700	20	20.2
64,400	15	20.8
59,700	10	22
54,400	7	25
51,300	5	28.3
43,000	3	35.2

CURVE showing decrease of resistance of SELENIUM CELL (5) at different distances from a 16cp. incandescent lamp.

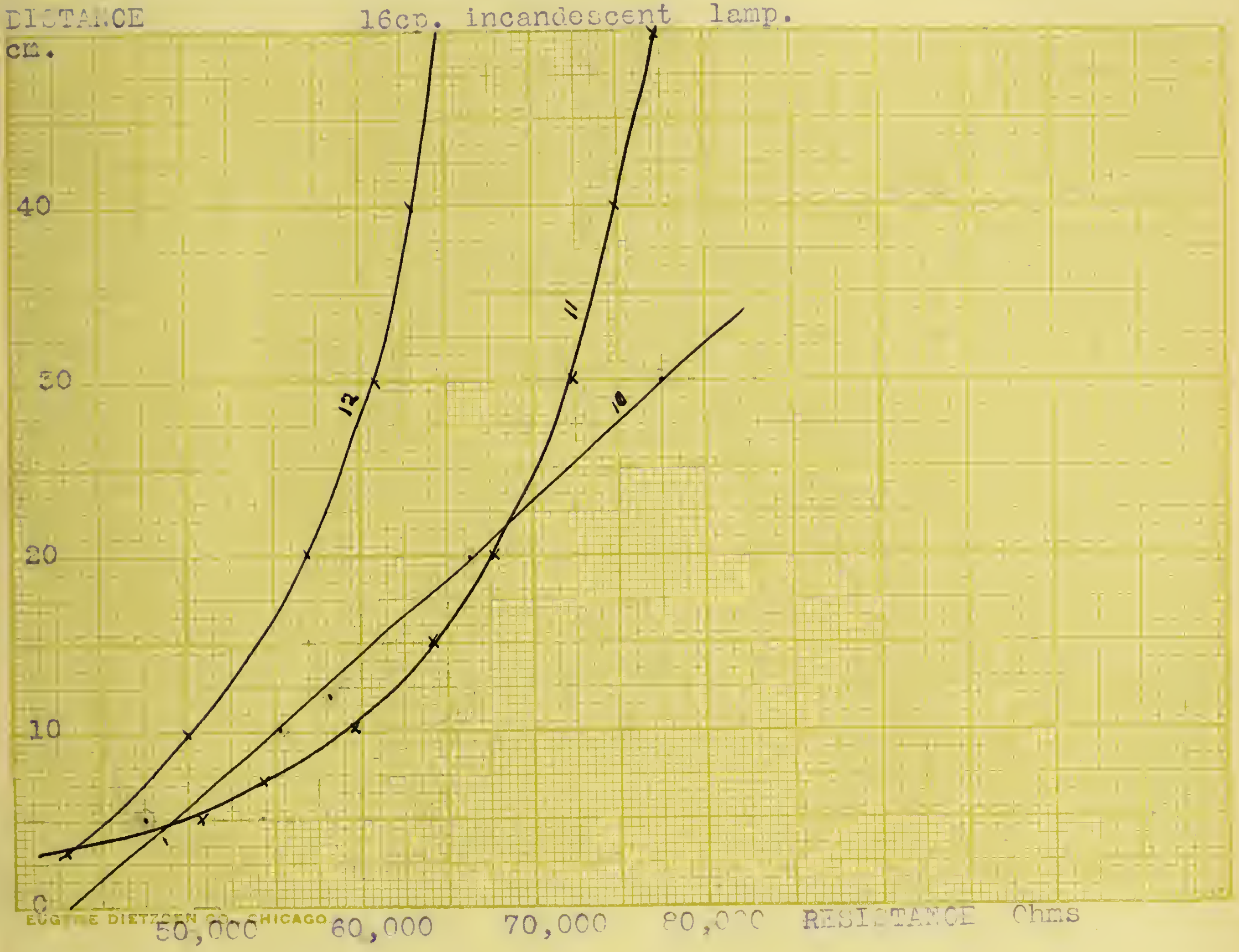


fig.9

RESISTANCE	DISTANCE cm.	TEMPERATURE
48,700	4	32.5
50,000	10	28.7
57,000	20	22.8
61,000	30	20.9
63,000	40	20.3
68,800		18.8
70,000		after 5 min.

Since heat produces a change of resistance as great as that produced by light, the question naturally suggested itself, would this increase of resistance with decrease of temperature continue to extremely low temperatures. With the idea of answering this question and of finding if light would affect the resistance at low temperatures, the writer subjected cell (5) to temperatures as low as -65 degrees C. by dissolving liquid carbonic acid gas in ether. The cell was placed in the ether directly. The room was darkened after the cell and ether had reached -60 degrees C. It was illuminated at stated intervals by an incandescent lamp placed 8 cm. from the cell. The readings are given below.

RESISTANCE ohms	TEMPERATURE	LIGHT
130,000	- 53° C.	off
116,000	- 56	off
110,000	- 58	off
100,000	- 59	off
94,000	- 60	off
90,000	- 60.5	off
86,000	- 61	off

RESISTANCE ohms	TEMPERATURE	LIGHT	
82,000	60° C.	off	
97,000	60.8	off	room darkened
110,000	?	off	
110,000	?	off	
114,000	?	off	
114,000	58 to 60.8	off	
21,000	58	on	
17,000	55	on	after 2 min.
17,000	53	on	" 4 "
15,800	57	on	" 2 "
15,700	61	on	" 2 "
15,600	61	on	" 2 "
15,500	61	on	" 2 "
22,400	61	off	" 1 "
24,400	61	off	" 1 "
25,500	61	off	" 1 "
25,600	61	off	" 1 "
26,100	?	off	" 1 "
26,800	?	off	1 min.
28,400	58	off	2 "
32,000	?	off	10 "
33,000	?	off	2 "
45,400	28	off	27 "
75,000	10	off	10 "
69,000	2	off	5 "
39,000	2	off	5 "
34,000	7	off	10 "

RESISTANCE ohms	TEMPERATURE	LIGHT	
25,000	14° C.	off	10 min.
26,000		off	10 "
20,000	18	off	15 "
20,000	18	off	5 "
20,000	18	off	10 "
17,900	18	on	1/2 "
14,000	18	on	2 "
15,000	?	off	
38,000	?	off	cell removed from ether and placed in air.
119,000	? room	after 4 hours.	
128,000	? room	"	1 day.
120,000	? room	"	3 "
119,000	? room	"	8 "

While these results do not seem to be entirely explainable there are a few things that are apparent. Light, at even such low temperatures as indicated, does change the resistance of the cell. The cell does not reach a stable resistance at once as it does at ordinary temperatures. Later results showed that while the low temperature had changed the resistance remarkably, it did not permanently change its sensitiveness to light. The light seemed to aid the low temperature, or the reverse, in reducing the resistance abnormally, as shown from the fact that the resistance fell from 114,000 ohms to 21,000 ohms as soon as the light was turned on.

But what conclusions are we to draw from all this data? The selenium cell changes its resistance very remarkably and very similarly when illuminated, when heated, when in the

presence of hydrogen peroxide, and when subjected to pressure. There is another class of agents which by some have been found to decrease the resistance, but these are so small in comparison with the former that they may not be considered in seeking for an explanation of the behavior of the selenium cell. Those things which decrease the resistance very much, with the probable exception of increase of voltage(or current), very likely decrease the resistance for the same reason.

The theory that has been most generally accepted as to the cause of decrease of resistance, has been that of Bidwell. He said that it was due to a selenide, which was found more or less in every selenium cell, and which made the cell a better conductor when the light fell upon it. In the light of investigation up to the present time, it seems that we are safe in saying that a selenide is not the cause.

Another theory has been given, that light produces crystallization, and since some kind of crystals conduct better than others the change of resistance is due to the formation of crystals in unstable equilibrium. But ordinarily pressure does not form any kind of crystals in any substance.

Another theory is that in the selenium cell there is a form of selenium called metallic, which conducts electricity well and which is a sort of solution with the non-conducting selenium. Light causes the metallic selenium to make better contact and thereby reduces the resistance. So far as the pressure is concerned, this theory might suffice. However the theory would have to be remodeled to accord with other facts.

The theory that led the author to try the effect of

pressure was, that the change of resistance was due to variable contact of the selenium with the electrodes. There are perhaps four reasons for thinking that this is the case. The change of resistance is such as would warrant contact differences. The coefficient of expansion of selenium is about seven times that of the ordinary metals used as electrodes. Thus any slight change of heating would produce a change in contact. Wherever the selenium peels off of the electrodes, one notices a thin layer of black deposit, which might aid in a variable contact. The change of resistance with pressure is what one would expect of the resistance were changeable because of contact differences. Carbon particles behave very similarly under pressure. The fact that the resistance decreases with increase of voltage is in harmony with the theory of variable contact. But until other investigations are carried on the author is by no means prepared to say that the last named theory is the true one. In fact there are reasons for thinking that it is not the true one.

However it is safe to conclude that the change of resistance is due either to contact differences or to a dynamic change in the selenium.

This work was carried on under the direction of Professor A. P. Carman, to whom the author is indebted for his suggestions and for his continual interest in the progress of the work.

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